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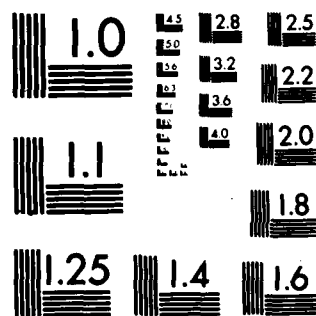
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On the Photoassisted Hydrogen Production
from Titania and Water

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S. Sato and J. M. White

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<p>When TiO_2, reduced by H_2 or CO, is placed in an ambient of gas phase water and illuminated with band gap light, H_2 is evolved. Adding a small amount of O_2 completely retards this reaction. A dark reaction of reduced TiO_2 with water to form H_2 also occurs at temperatures above 200°C. These results show that H_2 evolution is not the result of catalytic water photolysis but a photoassisted reaction of water with oxygen vacancies produced by the reduction.</p>		

On the Photoassisted Hydrogen Production
from Titania and Water*

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Abstract

When TiO_2 , reduced by H_2 or CO , is placed in an ambient of gas phase water and illuminated with band gap light, H_2 is evolved. Adding a small amount of O_2 completely retards this reaction. A dark reaction of reduced TiO_2 with water to form H_2 also occurs at temperatures above 200°C . These results show that H_2 evolution is not the result of catalytic water photolysis but a photoassisted reaction of water with oxygen vacancies produced by the reduction.

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Introduction

The photodecomposition of water over heterogeneous catalysts containing compound semiconductors has recently received considerable attention. Some works involve the use of semiconductors alone for achieving this and the results and their interpretation are the subject of some disagreement. Schrauzer and Guth¹⁾ concluded that water adsorbed on TiO_2 or Fe_2O_3 -doped TiO_2 was catalytically photolyzed in their system, whereas Van Damme and Hall²⁾, on the basis of finding only a trace of H_2 , concluded that H_2 formation arose from the non-catalytic photodecomposition of hydroxyl groups originally present on TiO_2 . Kawai and Sakata³⁾, on the other hand, found that D_2 was formed in the dark when gaseous D_2O was contacted with TiO_2 reduced by CO under UV irradiation. The evolution of D_2 was accelerated by illumination and continued even after evacuating D_2O , but no O_2 was observed. The acceleration was ascribed to the photodecomposition of D_2O over TiO_2 on the assumption that oxygen formed was held at the TiO_2 surface. This assumption is based on the fact that O_2 as well as H_2 was formed by the addition of RuO_2 , a good electrode material for O_2 evolution, to TiO_2 . Rao et al.⁴⁾ have recently reported that H_2 and H_2O_2 are produced when reduced TiO_2 (in flowing H_2 for ~ 6 hr at 700-800°C) is suspended in liquid water and illuminated in bubbling N_2 . Unreduced TiO_2 produces neither H_2 nor H_2O_2 .

We have already reported that platinized TiO_2 is a suitable catalyst for the photolysis of water to H_2 and O_2 but TiO_2 alone is not.⁵⁾ Moreover, we found that reduced TiO_2 produces H_2 when illuminated in the presence of gaseous or liquid water as observed by Kawai and Sakata³⁾ and Rao et al.⁴⁾, but we concluded, in agreement with Van Damme and Hall²⁾, that this H_2 production is non-catalytic. However, our results require somewhat different interpretation. This brief paper presents the experimental results and

our interpretation of them, the latter relying heavily on a model for the energy band diagram of illuminated TiO_2 .

Experiments and Results

The experimental apparatus and procedures have been described elsewhere⁵⁾. TiO_2 (MCB, anatase) was reduced in flowing H_2 (or CO) under various conditions, cooled in H_2 or CO and stored in air. Reduced TiO_2 (0.25g) was spread on the flat bottom of a quartz reaction cell and outgassed at 200°C for ~ 3 hr. After introducing water vapor at room temperature, the sample was illuminated by a 200 W high-pressure Hg lamp and the products were analyzed by a mass spectrometer.

In every case studied, only H_2 was observed in the gas phase and its formation rate dropped to almost zero after a few hrs of illumination. The maximum amount of H_2 formed increased with the reduction temperature and time and it was larger for H_2 -reduced TiO_2 than for CO-reduced samples prepared under the same conditions. The results described below were obtained for H_2 -reduced TiO_2 . For substrates reduced at temperatures above 700°C , H_2 was formed even in the dark in agreement with Kawai and Sakata³⁾ but its formation stopped within 30 min. When D_2O instead of H_2O was used, the products were dominated by D_2 . Since the amount of HD formed did not exceed the value expected from the isotopic purity of D_2O , the hydrogen evolved is believed to come from water added and not from pre-existing surface hydroxyl groups. Support for this also comes from the facts that no increase in HD was observed when D_2 (0.12 Torr) was added to the H_2O reduced TiO_2 system under illumination and that no products were formed when TiO_2 samples were illuminated in vacuo.

Light of energy less than the band gap of TiO_2 produced no H_2 , suggesting that photogenerated electrons and/or holes play an important role. The addition of O_2 (3.2×10^{-3} Torr) completely inhibited H_2 formation and its pressure dropped by a factor of 2 after 1 hr. of illumination. The

addition of ^{13}CO (0.25 Torr), on the other hand, had no effect and no $^{13}\text{CO}_2$ was observed. This is significant since CO is oxidized over TiO_2 in the presence of band gap light and oxygen.

When reduced TiO_2 was immersed in liquid water and illuminated, the amount of H_2 formed was larger than observed in the gas phase process. The liquid water- TiO_2 system was prepared by cooling the bottom of the reaction cell to 0°C in order to cryogenically pump water from the reservoir to the cell. After the sample was covered with 0.2-0.3 ml of water, the cell was warmed to $\sim 23^\circ\text{C}$ and then illuminated. The results are shown in Fig. 1 for variously reduced TiO_2 samples. Just as in the gas phase process, the H_2 evolution rate dropped to zero after a few hrs. and no O_2 was detected. The TiO_2 sample reduced at 750°C for 4 hr produced $\sim 1.3 \times 10^{-2}$ Torr ($0.13 \mu\text{mole}$) of H_2 in the dark (the pressure at time zero of curve (a) in Fig. 1 is due to this) and H_2 formation was accelerated by illumination.

Although the formation of H_2O_2 was not checked in our experiments, its concentration is limited by photodecomposition to O_2 and H_2O over TiO_2 . Rao et al.⁴⁾ observed that the addition of H_2O_2 ($\sim 5 \mu\text{mole}$) to their reaction mixture (700 ml) followed by 1 hr of illumination brought about a two-fold decrease in the H_2O_2 concentration. This implies that the maximum achievable concentration of H_2O_2 over illuminated TiO_2 is very low, less than $4 \mu\text{mole/l}$. Applying this to our system, $1 \times 10^{-3} \mu\text{mole}$, at most, of H_2O_2 could exist in the water. This is much less than the amount of H_2 formed ($>0.1 \mu\text{mole}$).

In addition to the above results, we find that H_2 is also formed when reduced TiO_2 samples are heated in gaseous water at temperatures higher than 200°C . The H_2 formation rate in this thermal reaction is proportional to $(p_{\infty}^{\text{H}_2} - p^{\text{H}_2})$, where $p_{\infty}^{\text{H}_2}$ is the maximum H_2 pressure and p^{H_2} the H_2 pressure at time t . The time dependence can, therefore, be described by the first order

equation:

$$\log (p_{\infty}^{\text{H}_2} - p^{\text{H}_2}) = - kt$$

where k is the rate constant. Fig. 2 shows plots of this relation for two sets of thermal reaction data. These data are consistent with a mechanism in which water reacts with oxygen vacancies of TiO_2 at a rate proportional to their concentration. The activation energy of the thermal reaction is about 24 Kcal/mole. It is noteworthy that the H_2 formation rate in the liquid water-illuminated TiO_2 system also depends on temperature and the activation energy is about 15 Kcal/mole between 0 and 23°C. The photo-processes, however, do not obey a first order equation.

Discussion and Conclusions

All of our photo results are consistent with a mechanism in which a reaction between H_2O and oxygen vacancies of reduced TiO_2 is photoassisted by the production of electron-hole pairs in the solid. This reaction is thermodynamically downhill and not catalytic.

The reduction (doping) of TiO_2 , however, is important in the preparation of active Pt/TiO_2 catalysts^{5,6)} and the TiO_2 electrodes of photoelectrochemical (PEC) cells⁷⁾, even though the oxygen vacancies are photo-oxidized by water. We assume that the bulk oxygen vacancies are retained during the photolysis of water and the active materials therefore have a relatively high conductivity. Ease of photogenerated electron transport from TiO_2 to Pt (or other cathode materials) and photochemical activity increase with conductivity. The position of the Fermi level and the thickness of the space charge layer of TiO_2 will also be affected by doping.

The fact that TiO_2 alone is inactive for water photolysis can be described in terms of the energy band diagram of illuminated TiO_2 ⁸⁾. According to a recent study⁹⁾ in this area, the flat band potential (electron Fermi level) of TiO_2 (rutile) is about 100 mV more negative than the H^+/H_2 redox potential. This implies that the water photolysis in PEC cells with a TiO_2 photoanode is energetically possible under open circuit conditions. However, there are some potential drops, for example, across the Helmholtz layer, so that the overvoltage available for H_2 evolution becomes lower. Even if anatase has a somewhat more negative flat band potential than rutile¹⁰⁾, the overvoltage would be too low for efficient evolution of H_2 at the TiO_2 surface¹⁰⁾. Similar overvoltage requirements for the reduction of protons are found with SrTiO_3 ¹¹⁾. Consequently, these semiconductor catalysts show increased photocatalytic activity for water decomposition when a material, such as Pt, is added which readily evolves H_2 at a lower overvoltage.

In passing, we note that the maximum amount of H_2 (1 μ mole) produced thermally exceeds that observed in the photoreaction (~ 0.2 μ mole). This difference is readily accounted for since in the photoprocess not all of the surface is illuminated.

To summarize, in the process proposed here, water reacts slowly with surface oxygen vacancies to evolve H_2 and remove the vacancies by filling them with oxygen or hydroxyl species. This is a non-catalytic process but is significantly accelerated by band gap irradiation. Bulk oxygen vacancies are retained during the photoprocess. Experimental support for this proposal comes from isotope tracing, the effects of reduction temperature and time, and the effects of added O_2 and CO . In the photoprocess, photogenerated holes probably oxidize water to produce some oxygen containing species which react with the oxygen vacancies at the surface.

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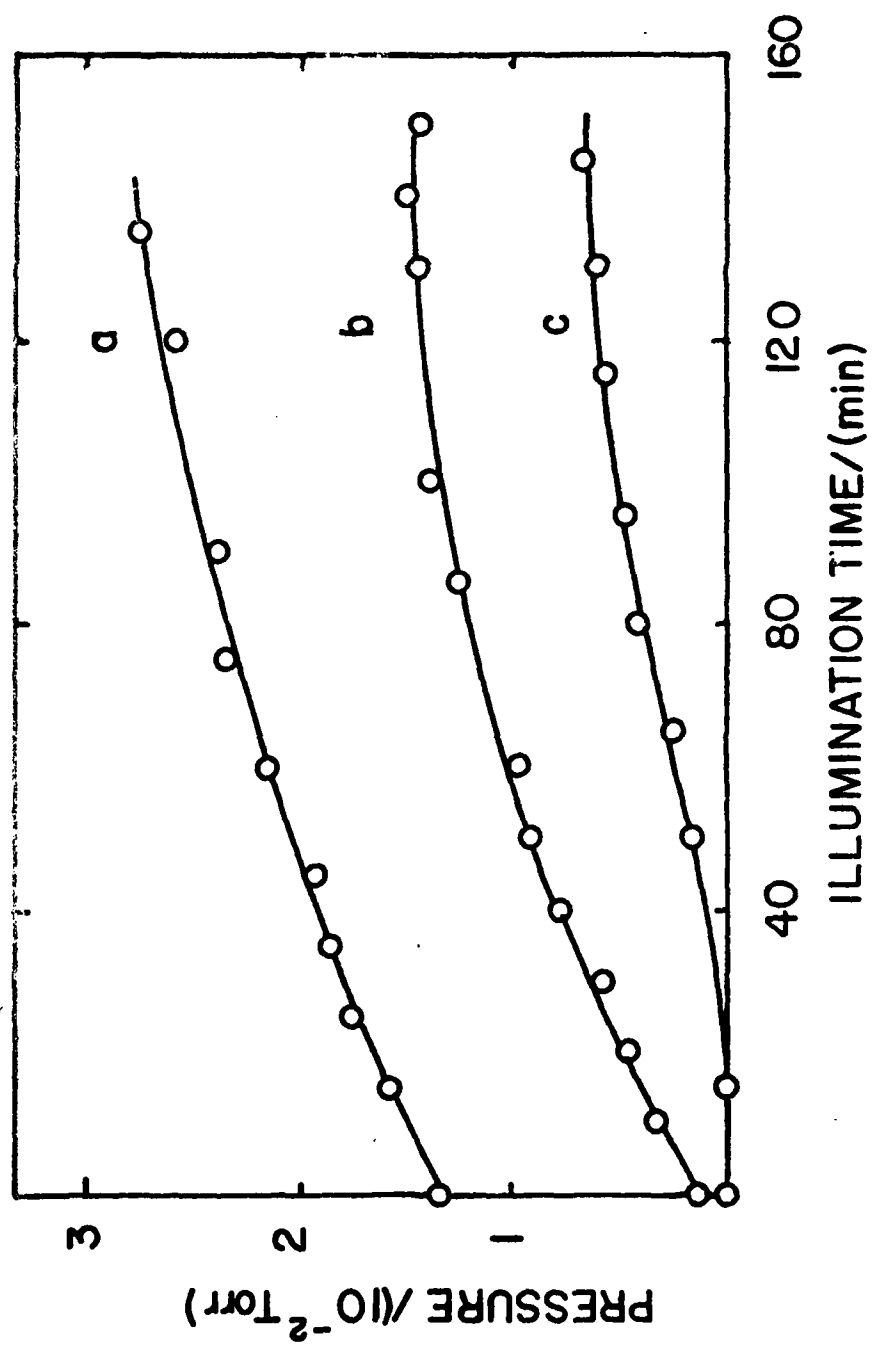
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Figure 1

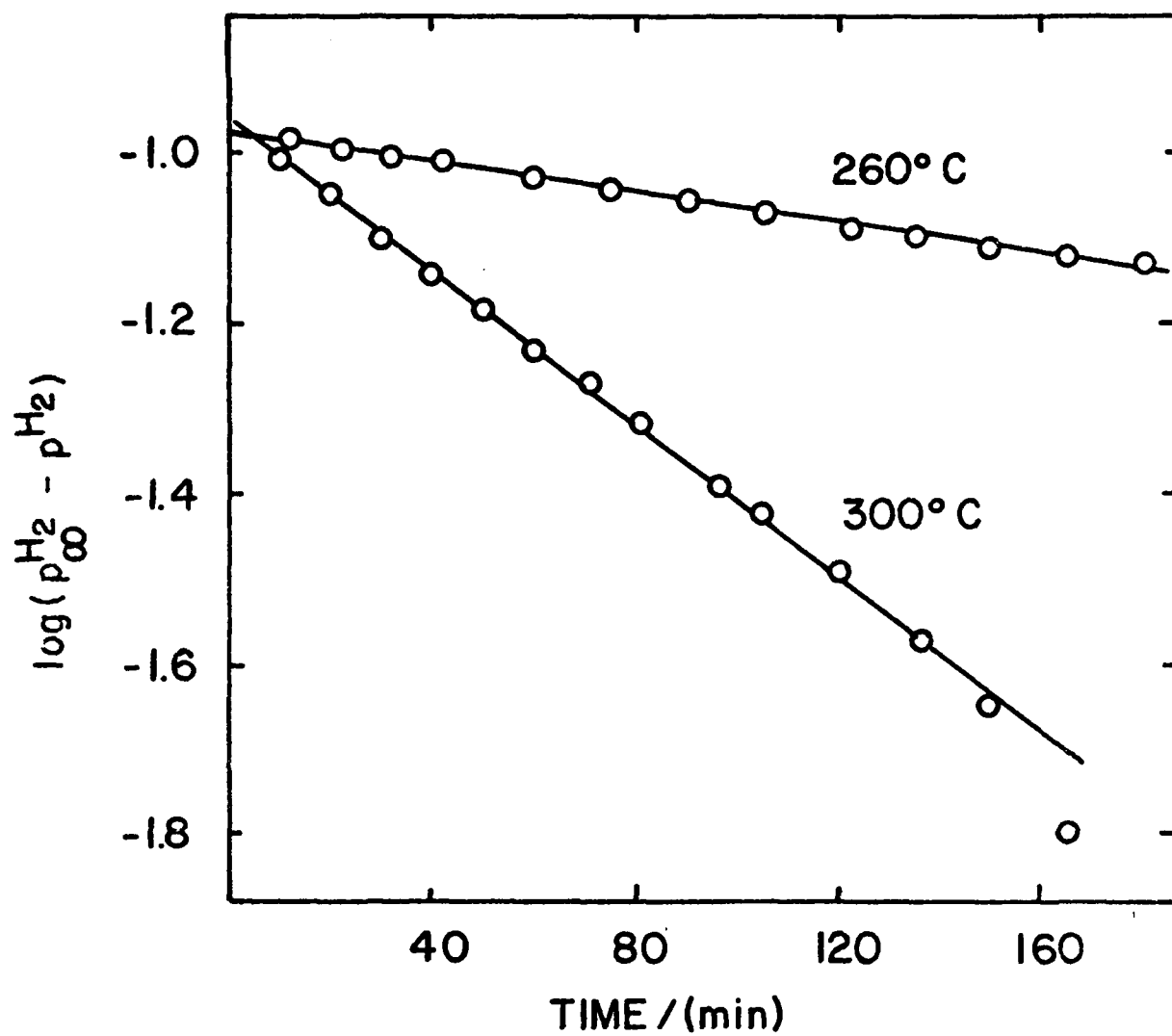
Evolution of H_2 from illuminated, reduced TiO_2 immersed in liquid water: (a) TiO_2 reduced by H_2 at $750^\circ C$ for 4 hr; (b) at $700^\circ C$ for 6 hr; (c) at $600^\circ C$ for 3 hr. (0.1 Torr = 1 μ mole).

Figure 2

First order plots of H_2 pressures ($p_{\infty}^{H_2} - p^{H_2}$) during the reaction of reduced TiO_2 with gaseous water (~ 24 Torr) at $260^\circ C$ and $300^\circ C$ in the dark. TiO_2 was reduced by H_2 at $700^\circ C$ for 6 hr.
 $p_{\infty}^{H_2} = 0.108$ Torr.



Sato/White Fig. 1



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